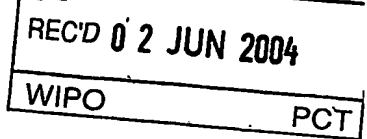




INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

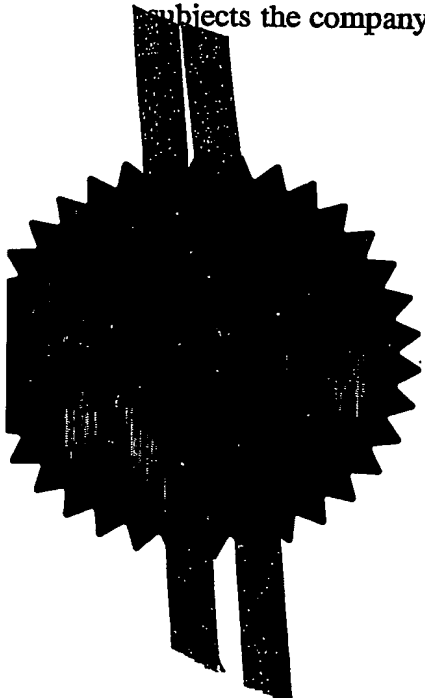


I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Andrew Gorse

Dated

24 May 2004

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Patents Form 1/77

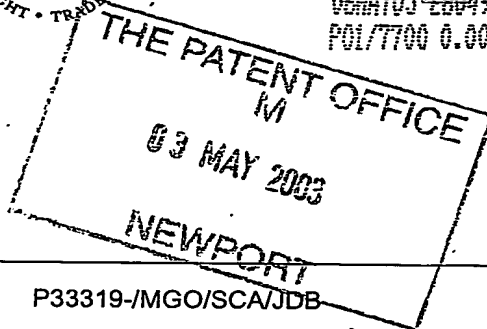
Patent Act 1977
(Rule 16)



05MAY03-ED04921-3 D02884
POL/7700 0.00-0310281.1

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

P33319-/MGO/SCAJDB

2. Patent application number

(The Patent Office will fill in this part)

0310281.1

8 MAY 2003

3. Full name, address and postcode of the or of each applicant (underline all surnames)

The Robert Gordon University
Schoolhill
Aberdeen
AB10 1FR

7343072001

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

"A Membrane Apparatus and Method of Preparing a Membrane and a Method of Producing Synthetic Gas"

5. Name of your agent (if you have one)

Murgitroyd & Company

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Scotland House
165-169 Scotland Street
Glasgow
G5 8PL

Patents ADP number (if you know it)

1198015

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Patents Form 1/77

9. 1. the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description	20 ✓
Claim(s)	-
Abstract	-
Drawing(s)	7 ÷ 3 ✓

10. If you are also filing any of the following, state how many against each item.

Priority documents	-
Translations of priority documents	-
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	-
Request for preliminary examination and search (Patents Form 9/77)	-
Request for substantive examination (Patents Form 10/77)	-
Any other documents (please specify)	-

11. I/We request the grant of a patent on the basis of this application.

Signature Murgitroyd & Co Date 2 May 2003
Murgitroyd & Company

12. Name and daytime telephone number of person to contact in the United Kingdom James D Brown 01224 706616

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

1 A Membrane Apparatus and Method of Preparing a
2 Membrane and a Method of Producing Synthetic Gas
3

4 The present invention relates to a membrane and a
5 method of preparing the membrane, the membrane being
6 particularly, but not exclusively, useful in
7 producing synthetic gas for use in Fischer-Tropsch
8 gas-to-liquids production in the oil and gas
9 exploration industry.

10
11 While offshore oil production has risen slightly in
12 recent years, natural gas (which mainly consists of
13 methane) production has seen a marked increase.
14 Natural gas is often extracted during the extraction
15 of liquid hydrocarbons, such as oil, from the ground
16 and is often undesirable due to the lack of
17 infrastructure to transport the natural gas to an
18 onshore location. The lack of infrastructure can be
19 explained by the physical nature of natural gas
20 which makes it difficult to transport safely and/or
21 efficiently in its basic gaseous state. As a result
22 the natural gas is often flared (ignited) causing

1 economic waste and environmental concern. It would
2 therefore be desirable to either convert the natural
3 gas into some other substance which can be
4 transported easily, or transport the natural gas in
5 a liquid state. In this way, new field development
6 will be more financially viable through the use of
7 the extensive infrastructure and technology already
8 in place in the offshore industry for transporting
9 liquid hydrocarbons.

10
11 It is known to transport natural gas as a Liquid
12 Natural Gas (LNG) in highly pressurised containers,
13 onboard vessels which have been adapted for such
14 purposes. However, this has many disadvantages
15 including; the need for expensive pressurising
16 equipment which is difficult to scale down to suit
17 smaller production fields, loss of gas during
18 transportation ("boil-off"), danger posed in transit
19 to vessel and crew by high pressure, highly
20 flammable gases and the requirement to depressurise
21 the LNG into a usable gaseous state at the customer
22 end.

23
24 It is considered that a better way of utilising
25 offshore produced natural gas (CH₄) is to convert
26 it, on or in close proximity to the offshore
27 production platform, into synthetic gas (syngas)
28 which can in turn be used to produce gases, fluids
29 and chemicals such as methanol, ammonia and
30 importantly, crude oil that can be readily pumped
31 through the same pipelines as the produced oil.

1 Syngas comprises a mixture of carbon monoxide (CO)
2 and hydrogen (H₂).
3

4 By way of background information to the reader,
5 conversion of syngas to liquid hydrocarbon is a
6 chain growth reaction between carbon monoxide and
7 hydrogen on the surface of a heterogeneous catalyst.
8 The catalyst is either iron or cobalt based and the
9 reaction is highly exothermic. The temperature,
10 pressure, and catalyst determine whether a light or
11 heavy syncrude is produced. For example at 330°C
12 mostly gasoline and olefins are produced whereas at
13 180°C to 250°C mostly diesel and waxes are produced.
14 There are two main types of Fischer-Tropsch
15 reactors. The vertical fixed tube type has the
16 catalyst in tubes that are cooled externally by
17 pressurised boiling water. In large plants, several
18 reactors arranged in parallel may be used,
19 presenting energy savings. Another process uses a
20 slurry reactor in which pre-heated syngas is fed
21 into the bottom of the reactor and distributed into
22 the slurry which consists of liquid wax and catalyst
23 particles. As the syngas bubbles upwards through
24 the slurry, it is diffused and converted into more
25 wax by the Fischer-Tropsch reaction. The heat
26 generated is removed through the reactors cooling
27 coils where steam is generated for use in the
28 process. Again by way of background information to
29 the reader, this is shown in Fig. 7.
30

31 It is known in the art that a reactor with
32 relatively dense ceramic membranes that conduct

1 oxygen can be used for syngas production (e.g. WO
2 98/48921 and WO 01/93987). These membranes generate
3 syngas by avoiding direct contact between the oxygen
4 and hydrocarbon feed, but this necessitates the use
5 of very high temperatures in order to achieve the
6 necessary oxygen flux. Moreover, being dense means
7 that the membrane has to be as thin as possible,
8 resulting in brittleness and crack formation, loss
9 of efficiency and reduced operating service life.
10 In some cases the membrane would need to be so thin
11 that it would be unable to support it's own weight
12 and therefore impossible to use in practice.

13

14 Cost effective natural gas (methane) conversion to
15 syngas for gas-to-liquids production would therefore
16 be an important commercial development.

17

18 According to a first aspect of the present invention
19 there is provided membrane apparatus comprising a
20 membrane and a catalyst, wherein the membrane is
21 adapted to allow passage of a first reactant from a
22 first chamber to a second chamber such that the
23 first reactant is activated by the catalyst upon
24 passage through said membrane.

25

26 According to a second aspect of the present
27 invention there is provided a method of preparing a
28 membrane comprising;

29 providing a membrane having pores extending
30 between at least two surfaces; and

31 applying a first coating to one of the surfaces
32 of the membrane.

1

2 Preferably, the membrane initially comprises an
3 inorganic support and more preferably comprises an
4 inorganic coarse porous support. Most preferably,
5 the membrane initially comprises a ceramic coarse
6 porous support such as alpha alumina.

7

8 Preferably, the first coating alters the said
9 surface of the support and more preferably, the
10 first coating roughens the said surface.

11 Preferably, the first coating selectively alters the
12 size, and more preferably, the diameter and
13 tortuosity of the pores. Preferably, the first
14 coating is applied by dipping the support into a
15 solution which may comprise a wash coat solution
16 such as a refractory metal oxide solution. In a
17 preferred embodiment, the wash coat solution
18 comprises Titanium Dioxide (TiO_2). Typically, the
19 first coating is applied to an outer surface which
20 may be an outer cylindrical surface of the support.

21

22 Typically, the method further includes the step of
23 applying a second coating to a second surface of the
24 support, said second surface preferably being an
25 inner surface of the support and more preferably
26 being an inner surface of a bore of the support.

27 The second coating preferably comprises a flux
28 control layer and more preferably the second coating
29 is an inorganic porous layer. Most preferably, the
30 second coating comprises a gamma alumina layer.

31 Preferably, the second coating is applied by dipping

1 the support into a solution which may comprise a
2 boehmite solution.

3
4 Typically, the method further includes the steps of
5 drying the support and heating/firing the support.
6 Typically, the dipping-drying-firing sequence of the
7 second coating may be repeated a number of times as
8 required.

9
10 Preferably, the method further includes the step of
11 applying a catalyst to a surface of the membrane.
12 Typically, the catalyst is applied to the inner bore
13 of the pores of the membrane. Typically, the
14 catalyst comprises a metallic or non-metallic
15 catalyst, and is more preferably a metallic active
16 catalyst. Most preferably, the catalyst comprises
17 active Rhodium. Preferably, the catalyst is applied
18 to the said surface by passing an osmotic solution
19 over the said first surface, which may be a first
20 side, of the membrane and a cationic or anionic
21 catalyst precursor solution over the said second
22 surface, which may be the other side of the
23 membrane, such that the catalyst is deposited on the
24 inner bore of the membrane pores. Preferably, the
25 osmotic solution comprises different electrolytes
26 and non-electrolytes in an aqueous solution at room
27 temperature. More preferably, the osmotic solution
28 comprises a sucrose solution.

29
30 Preferably, the method further includes the step of
31 heating the membrane to a relatively high
32 temperature and may include the further step of

1 passing Hydrogen through the membrane pores such
2 that calcination occurs.

3

4 Preferably, the support may comprise one or more
5 inner structures such as struts to increase the
6 surface area of the inner surface of the inner bore.

7

8 According to a third aspect of the present invention
9 there is provided a method of producing synthetic
10 gas comprising;

11 providing a membrane and a catalyst;

12 arranging for a first reactant to pass through
13 the membrane, into contact with the catalyst, from a
14 first chamber to a second chamber such that the
15 first reactant is activated by the catalyst upon
16 passage through said membrane.

17

18 Typically, the first reactant meets a second
19 reactant within the second chamber, at which point
20 the synthetic gas is formed.

21

22 Preferably, the membrane comprises a substantially
23 annular cylinder and more preferably, the first and
24 second chambers comprise a substantially cylindrical
25 cross section. More preferably, a sidewall of the
26 membrane separates the first and second chambers and
27 the second cylindrical chamber may be located within
28 the first cylindrical chamber.

29

30 Preferably, the second cylindrical chamber is
31 defined by an inner bore of the membrane.

32

1 Preferably, a portion of the membrane is permeable.
2 Alternatively, the entire membrane is permeable.

3

4 Preferably, the first reactant passes from the first
5 chamber through pores formed in the sidewall of the
6 membrane to the second chamber.

7

8 Alternatively, the second reactant passes from the
9 second chamber through the membrane to the first
10 chamber.

11

12 Preferably, the first reactant is oxygen and the
13 second reactant is a hydrocarbon. More preferably
14 the second reactant is methane. Typically, the
15 synthetic gas comprises carbon monoxide and
16 hydrogen.

17

18 An embodiment of the present invention will now be
19 described, by way of example only, with reference to
20 the accompanying drawings in which:

21

22 Fig. 1 is a transverse cross sectional
23 schematic view of a support of a membrane
24 apparatus in accordance with the present
25 invention;

26 Fig. 2A is a transverse cross sectional view
27 showing the support of Fig. 1 in more detail;
28 Fig. 2B is an end view of the support of Fig.
29 2A showing 'O' rings and cross sectional shape
30 of the support;

1 Fig. 3 is a transverse cross sectional view
2 showing the formation of layers in the membrane
3 of the membrane apparatus of Figs. 2A and 2B.
4 Fig. 4 is a temperature / syngas ratio plot
5 showing the optimal temperature required to
6 achieve the desired syngas ratio;
7 Fig. 5 is a feed ratio / syngas ratio plot
8 showing the optimal feed ratio required to
9 achieve the desired syngas ratio; and
10 Fig. 6 is a % Vol. N_2 / Conversion plot showing
11 conversion of CH_4 and O_2 at $750^\circ C$;
12 Fig. 7 is a schematic flow diagram providing
13 background information relating to Fischer-
14 Tropsch Gas-to-Liquids Technology.

15
16 A membrane apparatus 8 in accordance with the
17 present invention is shown in Fig. 1 and comprises a
18 membrane 10 based upon a tubular support 10, an
19 inner chamber or bore 14, and an outer tubular shell
20 16.

21
22 The tubular support 10 is in the form of an annular
23 cylinder having a sidewall 13 which is impregnated
24 with catalysts 12 which are distributed along the
25 length and around the circumference of the support
26 10 in order to form a membrane 10.

27
28 Referring to Figs. 2A, 2B and 3 the preparation of
29 the membrane 10 layers will now be described.

30
31 The process starts with an inorganic (preferably
32 ceramic) coarse porous support 10. Supports of this

1 nature are now widely available and a wide variety
2 of companies currently supply these base materials
3 and a preferred support 10 comprises an alpha-
4 alumina tube having 10mm outer diameter and a 7mm
5 inner diameter, typically having a pore size of
6 between 110 and 180 nm. The support 10 comprises a
7 porous middle portion 11 which is typically around
8 300 mm in length, and two remaining non-porous
9 portions 26 of about 25 mm in length at each end of
10 the membrane 10. The end portions 26 are made non-
11 porous by glazing them with a sealant, such as SiO_2 -
12 BaO-CaO at 1100°C .

13
14 A wash coat 28 is then applied to the outer
15 cylindrical surface of the support 10 by dipping the
16 support 10 into a substance such as TiO_2 . This wash
17 coat 28 dipping step roughens the outer cylindrical
18 surface of the support 10 and adds microporosity to
19 the walls of the membrane catalysts 12. (In
20 operation the rough surface of the wash coat 28
21 forces the oxygen particles (not shown) to convolute
22 around the raggedness of the wash coat 12 and serves
23 to improve mass transfer of the limiting reactant
24 (oxygen) to the catalytic sites - this results in
25 improved syngas yields).

26
27 An oxygen flux control layer 30 is then applied to
28 the inside surface of the inner bore 14 of the
29 support 10. This layer 30 should be inorganic to
30 enable operation of the membrane 10 at high
31 temperatures and may comprise a gamma alumina layer
32 derived from a boehmite (AlO(OH)) solution with a

1 concentration of 0.6 mol/L. The inner surface of
2 the support 10 is exposed to the boehmite solution
3 via dipping for about 2 minutes. The support is
4 then air-dried overnight and then heated to between
5 700 - 750°C at a rate of 1°C / min. It may be
6 necessary to repeat this dipping-drying-firing
7 sequence for up to a total of three cycles to
8 achieve the required gamma-alumina layer thickness
9 on the support 10.

10

11 The deposition of the catalysts 12 on the support 10
12 is achieved using an osmotic ionic exchange process,
13 which will now be described.

14

15 Osmotic Ionic Exchanged Catalyst Deposition:

16

17 The catalysts 12 will be prepared using either
18 cationic or anionic exchange using RhNO_3 or
19 $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ respectively in an organic medium
20 (0.2g/L) as precursors. Owing to the asymmetrical
21 character of the membrane as shown in Fig. 3 (i.e.
22 wash coat 28 + support 10 + gamma alumina layer
23 (boehmite) 30) different ways of introducing the
24 catalysts 12 to the support 10 will be compared. In
25 mode 1, the osmosis process will involve immersing
26 the outer surface of the partially modified membrane
27 10 in 6.0 molar sucrose solution, while either a
28 cationic or anionic solution is now circulated
29 through the inner bore 14 of the partially modified
30 membrane 10. This configuration is reversed in mode
31 2 with the immersion of the outer surface of the
32 partially modified membrane 10 now in a catalyst

1 precursor solution and the osmotic (sucrose)
2 solution now circulated in the inner bore 14 of the
3 partially modified membrane 10. The membrane 10 is
4 then washed using distilled water and subsequently
5 dried by blowing dry air either through the inner
6 bore of the now modified membrane 10 or across the
7 outer cylindrical surface.

8
9 Calcination (which involves heating the modified
10 membrane 10 to a very high temperature and then
11 passing Hydrogen through the modified membrane 10)
12 is then carried out under atmospheric pressure at
13 400°C for 2 hours. Metallic (active) Rh (the
14 catalyst 12) is obtained by reduction of Rhodium
15 ionic species using hydrogen at 400°C for 2 hours.

16
17 It should be noted that the inner bore of the
18 modified membrane 10 may have a number (such as
19 three as shown in Fig. 2B) of supporting struts 34
20 which increase the structural strength of the
21 modified membrane 10. In operation, the struts 34
22 also change the flow pattern of oxygen flowing
23 through the sidewall 13 of the membrane 10 by
24 reducing the opportunity for the methane flowing
25 through the inner bore 14 to pass directly through
26 the centre of the modified membrane 10 inner bore
27 without coming into contact with the modified
28 membrane 10 surface. The struts 34 also increase
29 the internal surface area per unit volume of the
30 modified membrane 10, and hence increase the
31 opportunity for activation, compared to a completely
32 hollow cross section.

1
2 The modified membrane 10 characteristics may now be
3 measured. This may be done by scanning electron
4 microscopy (SEM) to show the degree of filling of
5 the modified membrane 10 pore network and to
6 estimate the gamma alumina (boehmite) layer 30
7 thickness. The surface area of a material
8 determines many of its physical and chemical
9 properties, including water retention capacity and
10 reactivity with nutrients and contaminants. The BET
11 Surface Area Analyzer (named after S. Brunauer, P.H.
12 Emmet and E. Teller) can be used to estimate the
13 specific external surface of a solid by determining
14 the volume of a specific gas that is absorbed under
15 controlled conditions. The BET surface Area
16 Analyzer has typically been used in routine
17 characterisation of various membrane materials and
18 synthetic mineral analogs important in process
19 engineering systems. In the context of the present
20 invention, BET surface area analysis using nitrogen
21 adsorption is used to estimate the pore size
22 distribution in the modified membrane 10 and also to
23 indicate values of porosity and pore volume. Energy
24 Dispersive X-Ray Analysis (EDXA) surface analysis of
25 the modified membrane 10 is used to confirm whether
26 or not the modified membrane 10 forms a continuous
27 gamma alumina network and the extent of any defects.
28 It also provides elemental composition of the
29 catalysts 12 and its relative dispersion. X-ray
30 Photoelectron Spectroscopy (XPS) is then used for
31 chemical analysis of the modified membrane 10.

1 Multi-component selectivity can be obtained by
2 measuring the individual species concentration in
3 the feed and permeate respectively. Gas
4 permeability through the modified membrane 10 can be
5 measured by placing the end of the modified membrane
6 10 sample tightly against the ends of the outer
7 tubular shell 16, with a seal being formed
8 therebetween by 'O' rings 32. A gas connection (not
9 shown) of the outer tubular shell 16 is attached to
10 a source of constant pressure. The predetermined
11 pressure difference being used creates a stable flow
12 of gas through the sidewall 13 of the membrane 10
13 sample, and is used to measure the flow rate, which
14 is proportional to the gas permeability of the
15 modified membrane 10.

16
17 The location and operation of the modified membrane
18 10 in the membrane apparatus 8 will now be
19 described.

20
21 The inner bore 14 of the modified membrane 10 and
22 thus the membrane apparatus 8 forms a section which
23 is substantially sealed off from the outer chamber
24 or bore 22 which is provided by the annular space
25 between the outer cylindrical surface of the
26 modified membrane 10 and the inner cylindrical
27 surface of the outer tubular shell 16.

28
29 An oxygen (O_2) supply 18 is fed into the outer bore
30 22 at one end of the membrane apparatus 8, and a
31 natural gas (which mainly comprises methane (CH_4))

1 supply 20 is fed into the corresponding end of the
2 inner bore 14.

3
4 The partial pressure of the oxygen 18 is maintained
5 at a higher pressure than that of the methane supply
6 20, which results in the oxygen passing through the
7 pores (not shown) of the modified membrane 10 from
8 the outer bore 22 to the inner bore 14. Upon doing
9 so, the oxygen particles (not shown) come into
10 contact with the catalysts 12 present in the
11 sidewall 13 of the modified membrane 10, which
12 activates the oxygen particles (not shown) before
13 contacting the methane present in the inner bore of
14 the modified membrane 10. When the activated oxygen
15 particles (not shown) come into contact with the
16 methane particles (not shown), syngas is instantly
17 formed according to the following chemical
18 reaction:- $\text{CH}_4 + \text{O}_2^* \Rightarrow_{\text{catalyst}} \text{CO} + \text{H}_2$. The produced
19 syngas exits the membrane apparatus 8 from the other
20 end of the inner bore 14 due to the natural pressure
21 differential created by the methane supply 20, such
22 that a syngas flow 24 is created. Pneumatic control
23 of the oxygen supply 18 flow rate allows different
24 flow rates of the methane supply 20 to be used,
25 since an increase in the pressure of the oxygen
26 supply will result in a greater flux of oxygen
27 through the pores of the modified membrane 10.

28

29 Since, in the modified membrane 10, the catalysts 12
30 are highly dispersed, lower reaction temperatures
31 are feasible thereby reducing the propensity for
32 coke formation and subsequent deactivation of the

1 catalysts 12. The absence of coke formation
2 optimises catalyst usage whilst maintaining high
3 syngas selectivity. In the operation of the
4 membrane apparatus 8, additional catalysts (not
5 shown) may be inserted into the inner bore of the
6 modified membrane 10 as necessary to further enhance
7 the reaction. These additional catalysts (not
8 shown) are obtained by physically breaking another
9 sample of a modified membrane 10 into appropriate
10 particle sizes and inserting the particle sizes into
11 the test or operation sample.
12

13 In order to maintain consistency the performance and
14 stability of the membrane apparatus 8 must be
15 determined. This is done by conducting extended
16 experimental runs lasting at least 50 hours with the
17 modified membranes 10 themselves under reaction
18 conditions. Temperature profiles along and across
19 the permeation zone of the catalyst bed for various
20 flow rates are also considered as well as the
21 methane and oxygen conversions for a conventional
22 fixed-bed reactor and a membrane apparatus 8 system.
23 An estimation of the kinetic parameters will be
24 carried out in low methane conversion as well as
25 high methane conversion reactor operations. The
26 results of these tests enable various reaction rate
27 constants to be evaluated. Reaction rates measured
28 at various temperatures enable an estimate of the
29 activation energies associated with each reaction
30 stage.
31

1 Analysis of the reactants and products are analysed
2 using gas chromatography (GC) on-line using a 5 m
3 1/8 inch molecular sieve column to determine
4 methane, O₂, H₂ and CO. Any CO₂ will be analysed
5 using a separate 2 m long column of Porapak (RTM)
6 QS. In this analysis, a thermal conductivity
7 detector is also used. Water formed during the
8 reaction is condensed in an ice trap and further
9 removed by using a Drierite (RTM) trap.

10

11 Multi-component gas mixtures consisting of methane,
12 hydrogen, carbon dioxide, carbon monoxide and oxygen
13 are fed on one side of the modified membrane 10
14 (e.g. the outer bore 22) and the streams entering
15 and exiting the inner bore 14 will be analysed using
16 the Thermal Conductivity Detector (TCD) of a gas
17 chromatograph.

18

19 A mathematical model is then created which entails
20 writing a mass balance for the permeating species on
21 the outer bore 22 side, the equation for gas flux
22 across the membrane 10 and the chemical reaction
23 equation for each species. Basic assumptions such
24 as isobaric system and isothermal operation of the
25 membrane apparatus 8 are made in the mathematical
26 model development. Material balance is written for
27 every species and calculated over an arbitrary
28 volume element. Initially, the balances on the
29 radially mixed regions are made. In the axial
30 direction, viscous and diffusive flows will be taken
31 into account. In the radial direction, exchange of
32 material through the boundary layer (not shown) and

1 viscous flow are also incorporated in the
2 mathematical model.

3

4 The process of testing the modified membrane 10 for
5 methane partial oxidation characteristics will now
6 be described.

7

8 The modified membrane 10 is tested for methane
9 partial oxidation to synthesis gas in the membrane
10 apparatus 8. Experiments are run and comparison
11 made between the following scenarios:

12

13 i) Oxygen is fed into the outer bore 22 and
14 methane flows in the inner bore 14 (reaction
15 side); and

16 ii) Both oxygen and methane flow in the inner
17 bore 14 (reaction side).

18

19 In each case, values of oxygen and methane
20 conversions and the yields of hydrogen and carbon
21 monoxide are monitored.

22

23 Mode i):- since the oxygen and methane are separated
24 by the modified membrane 10, it will be possible to
25 study the pneumatic control concept which suggests
26 that convective flow of oxygen can inhibit back-
27 diffusion of the hydrocarbon (methane). Successful
28 application of this concept in the present invention
29 will require that the oxygen transmembrane flux to
30 match the requirements for selective oxidation. Gas
31 throttling can achieve this.

32

1 Mode ii), is similar to a conventional fixed-bed
2 process. Here at the membrane apparatus inlet 20,
3 the concentrations of oxygen and methane are
4 maximum, while at the outlet 24, the concentration
5 of oxygen and methane are minimum, so the catalyst
6 will not be efficiently utilised. Moreover, because
7 there is still oxygen present, some of the carbon
8 monoxide formed at the initial stages of the
9 reaction will react with oxygen to produce carbon
10 oxides such as carbon dioxide. This phenomena is
11 reflected in the product distribution analysis.

12
13 Other aspects to be investigated in testing the
14 membrane 10 include the effect of operating
15 temperature (Fig. 4), methane flow rate (Fig. 5) and
16 composition of syngas yield and selectivity (Figs. 4
17 and 6). From examination of Fig. 4 it can be seen
18 that an optimal temperature of around 750°C results
19 in the desired syngas (H_2/CO) ratio of 2. (It is
20 known in the art that the optimal syngas ratio for
21 use in gas-to-liquids conversion in the Fischer-
22 Tropsch process is 2).

23
24 The optimal feed ratio of methane to oxygen is
25 shown, in Fig. 5, to be 10, although reasonable
26 results which are relatively close to the desired
27 ratio of 2 are obtained at feed ratios of between 2
28 and 6 also.

29
30 In Fig. 6 it is shown that even for an 80% vol N_2
31 feed (and hence 20% O_2 feed) total oxygen conversion
32 takes place at a temperature of 750°C. This is

1 highly desirable since air essentially comprises
2 approximately 80% N₂ and 20% O₂, thereby negating the
3 need for an oxygen separation plant for this
4 reaction to take place. This clearly reduces both
5 the initial outlays and operating costs of
6 performing the reaction.

7
8 Modifications and improvements may be made to the
9 foregoing without departing from the scope of the
10 present invention. For example;

11
12 Though the apparatus and method described relates to
13 the production of syngas from the reaction between
14 methane and oxygen, a similar method and apparatus
15 could be used in the reaction of any light
16 hydrocarbon such as members of the alkane or alkene
17 group. Furthermore, the process and apparatus could
18 be used in any reaction where there are two
19 reactants which have constraints that make it
20 undesirable to mix them before the reaction has
21 taken place, such as flammability constraints.

22
23 It will be understood that the flux of oxygen could
24 be reversed by feeding the oxygen into the bore of
25 the modified membrane 10, and the methane into the
26 outer bore 22. However, in this case this
27 arrangement would be less desirable since the
28 methane may have impurities in it, such as H₂S,
29 which would poison the catalyst 12. Therefore
30 passing the oxygen through the modified membrane 10
31 is preferred.

1/7

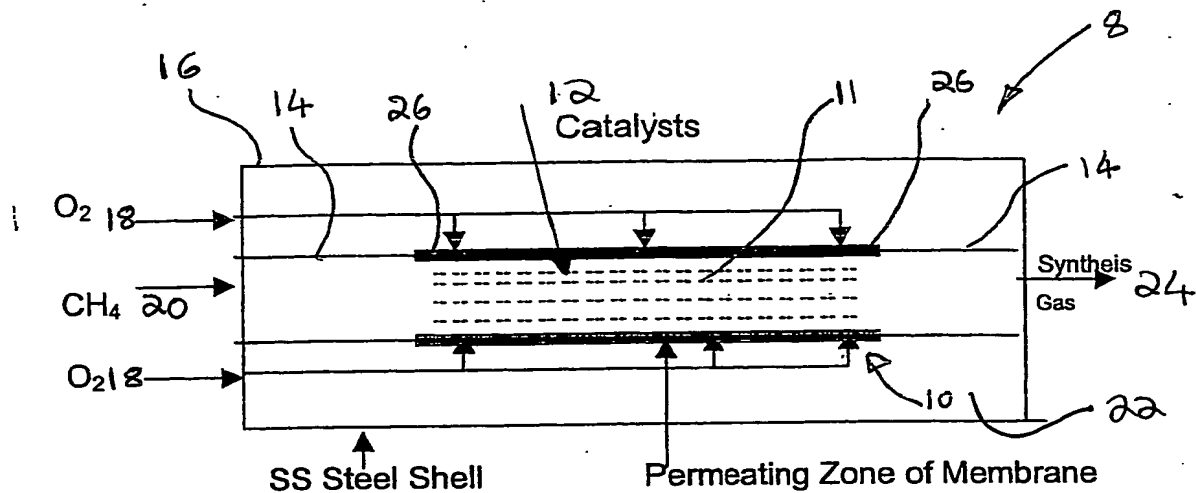


Figure 1. Schematic of the Novel Fischer -Tropsch Catalytic Membrane Reactor

Fig 2A

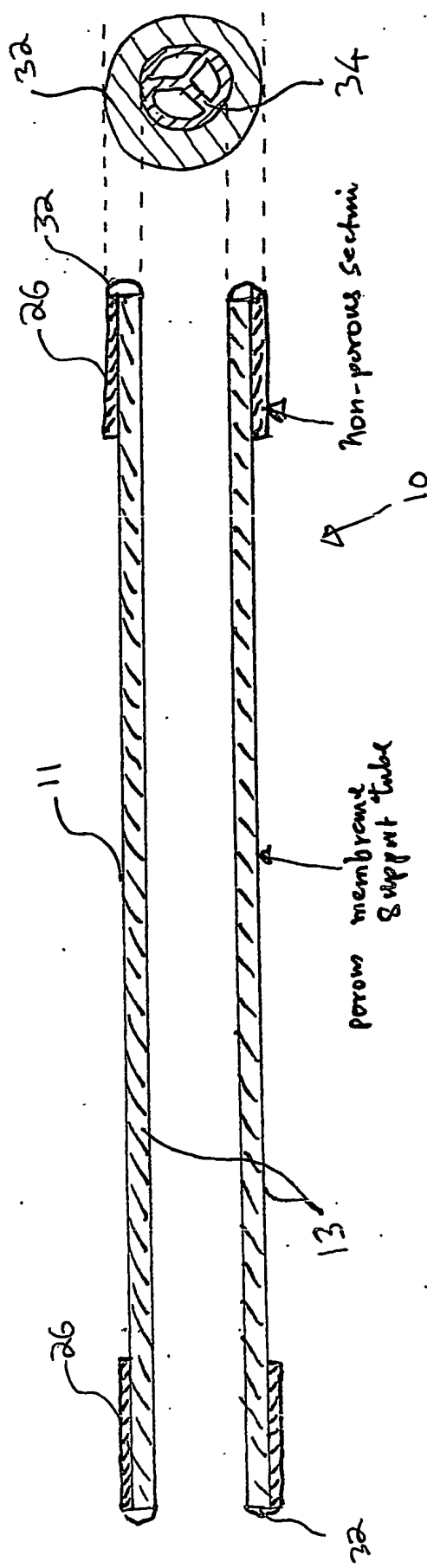
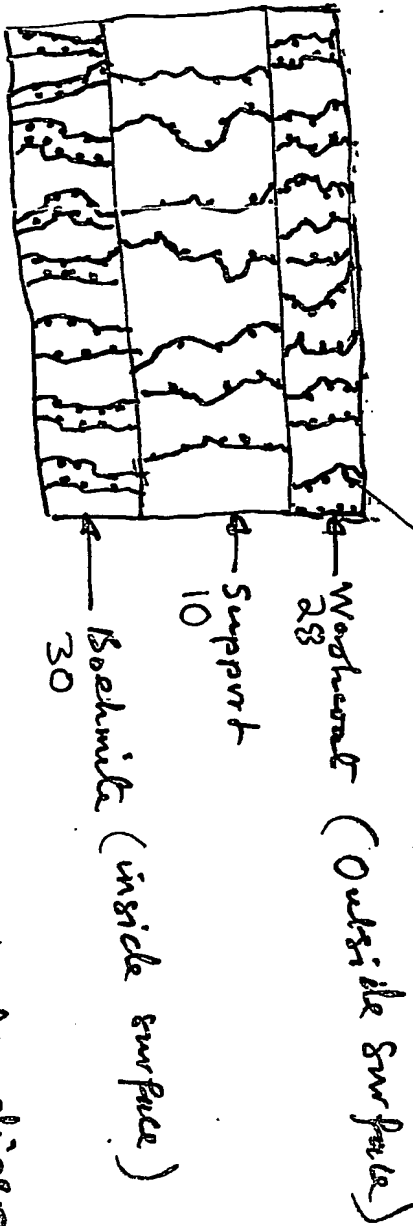


Fig 2B

2/11

Membrane Tube with non-porous ends

Fig 3



Typical Build-up of membrane layers indicating dispersing of Catalyst.

Fig 4

(CH₄/O₂) feed = 150/15

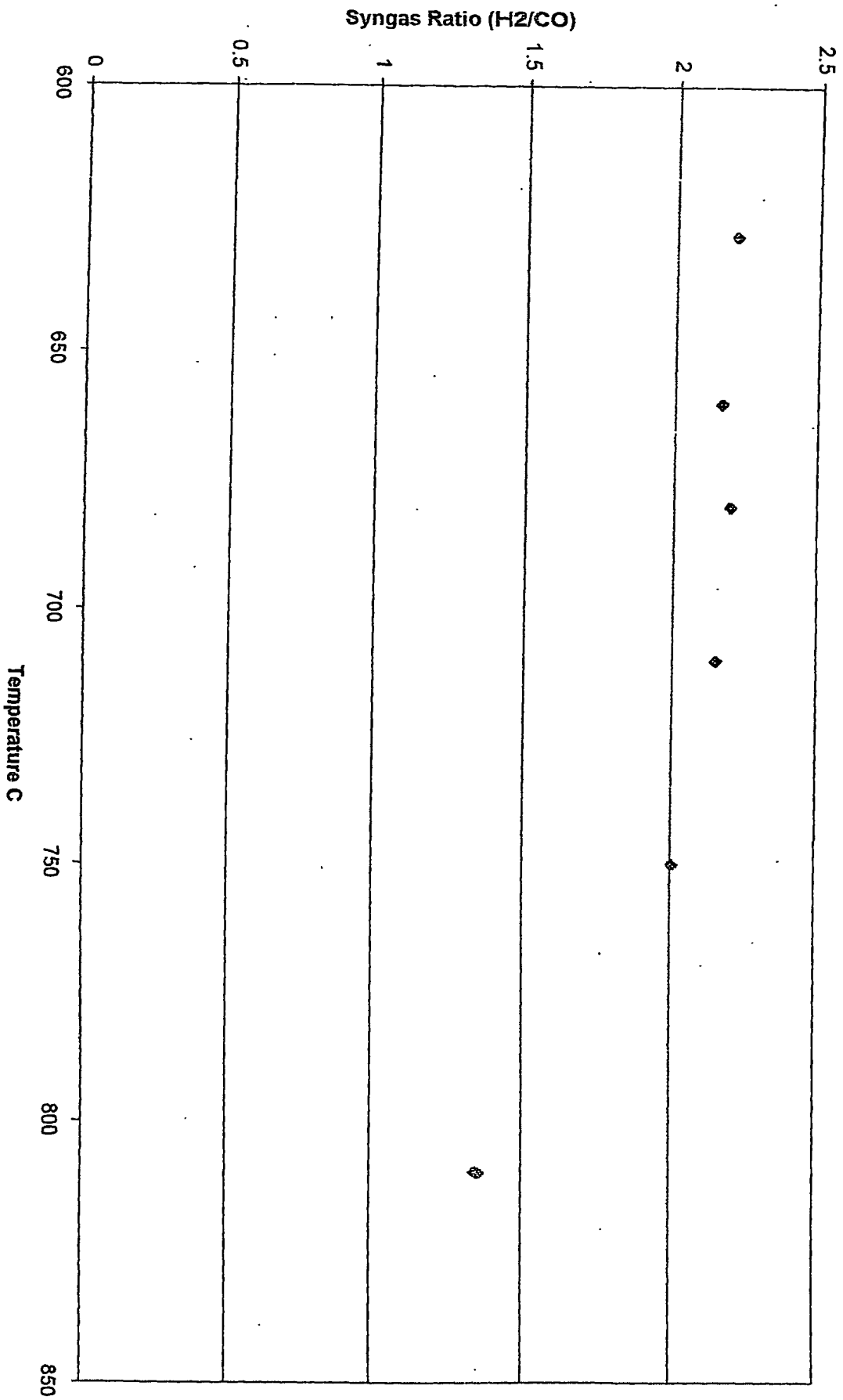


Fig 5

T=750 C

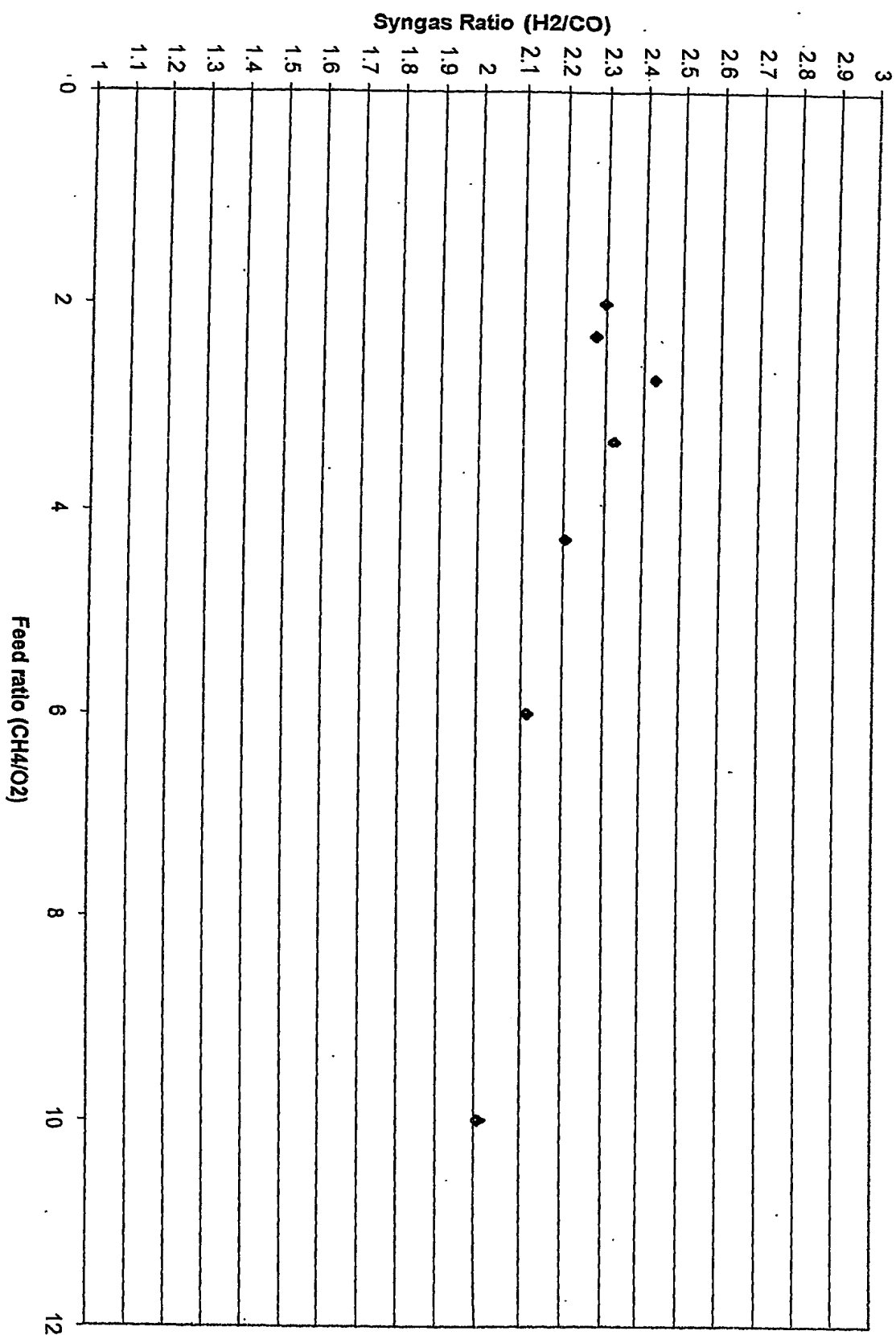
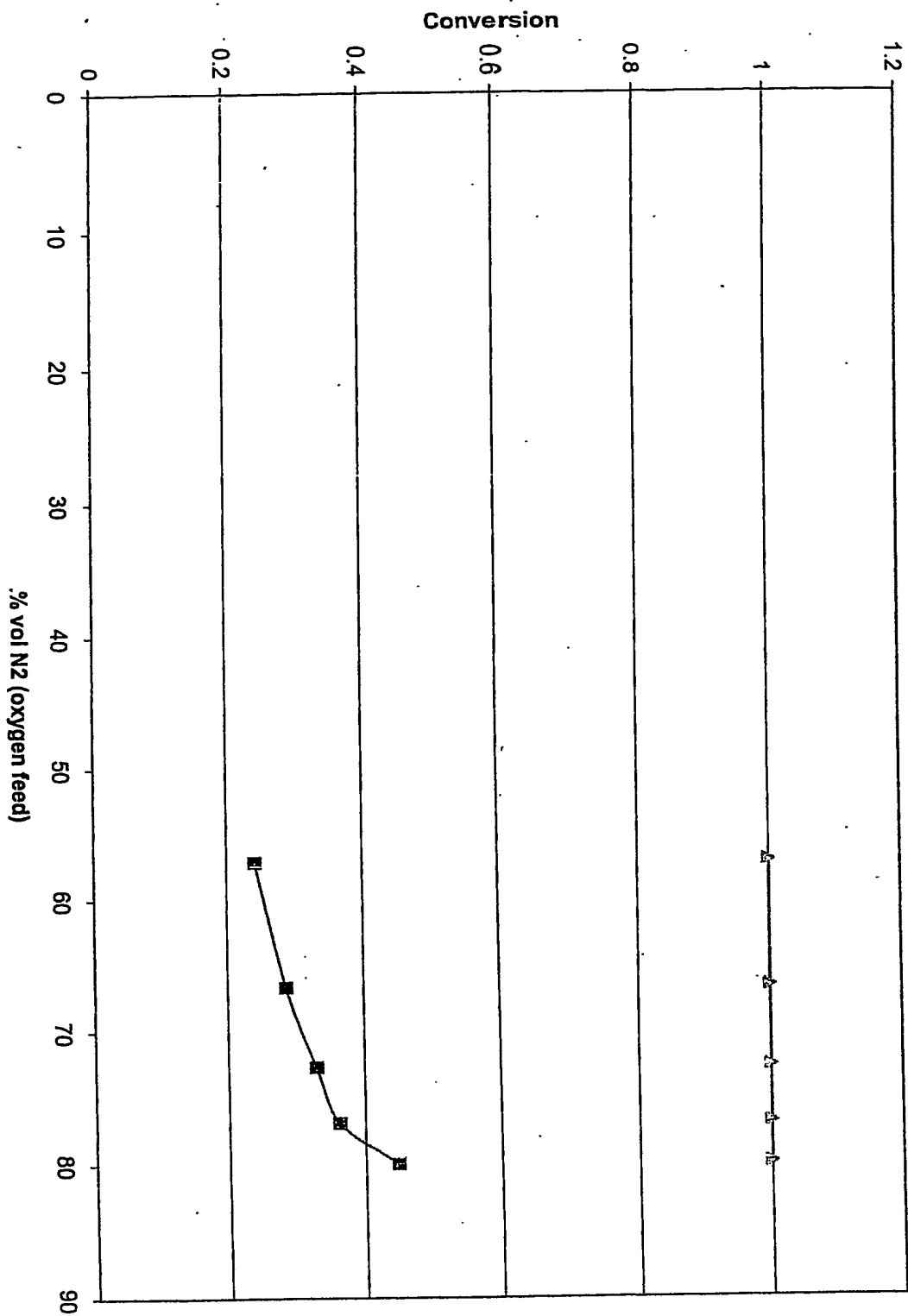


Fig 6

T = 750 C



—■— CH4 conversion
—▲— O2 conversion

7/7

Fig. 7

